Detail Analysis of the Mn *K*-edge in $La_{1-x}Ca_xMnO_{3+\delta}$ (x=0, 0.3, 1)

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Abstract No. igna1131
Beamline(s): **X18B, X19A**

Introduction: CMRs perovskites $La_{1-x}A_xMnO_{3+\delta}$ (A= Ca, Ba, Sr) are of interest due to their interesting electronic, magnetic, and structural properties as well as for their potential technological applications. Mn *K*-edge XANES is a powerful tool in identifying the possible electron configurations of Mn ions and in studying the effects of local magnetic ordering and local structural distortions.

Methods and Materials: Powder samples of $La_{1-x}Ca_xMnO_3$ (x=0, 0.3, 1) were prepared by the standard solid-state reaction. Mn *K*-edge XANES measurements were performed on the Beamlines X19A and X18B. In order to suppress the remaining La *L* edge oscillations the XAS spectra were collected in the fluorescent yield mode using a 13-element Ge detector with energy resolution ~180 eV. From three to six scans per sample were taken to improve the signal-to-noise ratio.

Results: Highlight We have considered *separately* the effects of magnetic ordering, lattice distortions, and charge disproportionation upon the shape of the Mn *K*-edge in $La_{1-x}Ca_xMnO_3$ (x=0, 0.3, 1).
Local structure: To study the lattice effect in the manganites we have performed single-electron calculations of the Mn *K*- edge in $La_{1-x}Ca_xMnO_3$ (x=0,0.3). The spectra were calculated in the real space using the formalism of multiple scattering (MS) of the photoelectron in a cluster of finite size. Main features at the absorption edge can be satisfactory reproduced. In the "metallic" phase of x=0.3 sample the edge is sharper than in the "insulator" phase, in good agreement with experimental data.
Magnetic ordering: We have performed spin-polarized Mn *K*- edge calculations for x= 0, 0.3, and 1. There are energy shifts between the spin-up and spin-down spectra for all compounds originating from the spin-dependence scattering of the photoelectron in the final states. Since the conventional Mn *K*-edge spectrum is given by a sum of spin-up and spin-down spectra: $XANES(E) = 0.5(XANES_{\uparrow}(E) + XANES_{\downarrow}(E))$ splitting for spin-up and spin-down XANES spectra will contributes to the broadening of the total spectrum. The energy shift at the half-height of the edge reaches the maximum of 1.1 eV in the "metallic" x=0.3 sample. The shifts of ~0.9 and ~0.5 eV are found in $LaMnO_3$ and $CaMnO_3$ roughly following the magnitude of the local magnetic moments on the Mn sites as observed by neutron-diffraction measurements.
Charge disproportionation: We can point out two features of the absorption edge that are related to the charge disproportionation: (i) a pre-edge peak at E~6542 eV and (ii) a feature B_3 that is ~6 eV above the absorption maximum. Calculated *K*-edge XANES spectrum has been obtained as a convolution product of the single-electron transition from the *1s* core-level to the unoccupied electronics states, $I(\omega)$, and the spectrum of many-body excitations in the electronic states in the presence of the *1s* core-hole, $S(\varepsilon)$ [1]. The excitation spectrum contains ~8% of spectral intensity in the peak that stands at +6.2 eV *above* the major peak and gives rise to the so-called *shake-up* transition. The inclusion of the excitation spectrum (i) introduces the additional broadening, (ii) rescales the absolute energy, and (iii) improves the overall agreement. In particular, the shake-up peak B_3 appears.

Conclusions: Experimental observation of the shake-up peak and Hamiltonian's parameters used in the calculations both imply that $LaMnO_3$ should be viewed as a charge-transfer-type insulator with a *substantial O 2p component in the ground state*. These findings contradict to the "intermediate" Mn valence and conventional DE mechanism both implying 3*d* character of doped states. We argue [1] that the disproportionation may be understood as a mixture of the charge-transfer many-body electronic configurations: $\alpha|3d^5\rangle + \beta|3d^4\rangle + \gamma|3d^5L\rangle + \delta|3d^6L^2\rangle + \varepsilon|3d^3\rangle + \zeta|3d^4L\rangle + \eta|3d^5L^2\rangle + \theta|3d^4L^2\rangle + \ldots$ coupled with spin and lattice degrees of freedom.

Acknowledgments: This work was supported in part by the Consortium for Advanced Radiation Source, University of Chicago. Data acquisition was done at the NSLS, which is supported by the US DOE under contract number DE-AC02-98CH10886.

References: [1] A.Yu. Ignatov, and S. Khalid, Phys. Rev. B**62** (to be published)